



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



0 198 558 B1

(11) Publication number:

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 07.04.93 (51) Int. Cl. 5: D01F 9/12, C08J 5/04,  
C08J 5/24, C04B 35/52,  
(21) Application number: 86200624.4 H01M 4/96  
(22) Date of filing: 14.04.86

(54) Method for the preparation of carbon filaments and carbon filaments obtained by the method.

(30) Priority: 15.04.85 US 723123

(43) Date of publication of application:  
22.10.86 Bulletin 86/43

(45) Publication of the grant of the patent:  
07.04.93 Bulletin 93/14

(64) Designated Contracting States:  
BE CH DE FR GB IT LI NL SE

(56) References cited:  
EP-A- 0 136 497  
DE-A- 2 615 523  
FR-A- 1 511 672

JOURNAL OF CRYSTAL GROWTH, vol. 66, no.  
3, May 1984, pages 632-638, Elsevier Science  
Publishers B.V., Amsterdam, Netherlands;  
G.G. TIBBETTS: "Why are carbon filaments  
tubular?"

(73) Proprietor: THE DOW CHEMICAL COMPANY  
2030 Dow Center Abbott Road P.O. Box 1967  
Midland Michigan 48640-1967(US)

(72) Inventor: Geus, John Wilhelm  
Gezichtsstraat 100  
NL-3723 GJ Bilthoven(NL)  
Inventor: Linowski, John Walter  
2455 Woodland Estates Drive  
Midland Michigan 48640(US)

(74) Representative: Smulders, Theodorus A.H.J.,  
Ir. et al  
Vereenigde Octrooilbureaux Nieuwe Parklaan  
97  
NL-2587 BN 's-Gravenhage (NL)

EP 0 198 558 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

**Description****Background of the Invention**

The invention relates to a carbon filament having a crystalline graphitic structure and a morphology defined by a fishbone-like arrangement of symmetrically stacked graphite layers along the axis of the filament and to a method for the preparation of said filament.

Carbon fibers are forms of carbon which are known in the art and which have a diameter of, normally, from 5 to 15 micrometers. They are flexible, light in weight, thermostable, and to a large extent, chemically inert, and they are good thermal and electrical conductors. Such carbon fibers are produced by carbonizing an organic polymer yarn, for example, of rayon or polyacrylonitrile to form a fiber built up from a multitude of fibrils. The most important parameter to characterize carbon fibers is the preferred orientation, i.e., the extent to which carbon or graphite microcrystallites are oriented parallel to the fiber axis. The thermal and electrical conductivity as well as the intrinsic tensile strength and Young's modulus increase with increased preferred orientation.

Carbon fibers can be divided into two categories, low-modulus fibers having a Young's modulus below about 140 g Pa and high-performance fibers having a Young's modulus above about 170 g Pa and having a very high tensile strength.

It is also known to prepare high-performance carbon fibers from polymer fibers such as polyacrylonitrile fibers by carbonizing the fibers and subsequently subjecting the fibers, in an inert gaseous atmosphere, to an elevated temperature. To endow the fibers with the desired high mechanical strength, they must be subjected to a tensile stress at the very high recrystallization temperature. Partly as a result of the mechanical force applied, the graphite layers in the fiber have their planes oriented parallel to the axis of the fiber.

It is apparent that the procedures required for the production of carbon fibers by presently known methods is very expensive. As a result, it has up till now only been possible for carbon fibers to be used in applications where the required amount of fibers is relatively small and the price of the finished product is not critical. For large scale commercial applications, however, the cost of producing carbon fibers in large quantities is still prohibitive.

In a more recent development a new method of manufacture of graphite fibers has been disclosed in which the fibers are produced at a high yield by the pyrolysis of a hydrocarbon gas, U.S. Patent No. 4,391,787 (G. G. Tibbetts). In this method, gaseous

methane, or the like, is contacted with a chromium oxide film on one side of a thin hydrogen-permeable wall, while concurrently dissolving hydrogen into the opposite side of the permeable wall, and heating the wall and the gas to a temperature of from 925° to 1075° to form on the first wall surface graphite fibers from the carbon containing gas.

An article of the same scientist in the Journal of Crystal Growth, 66 (1984), 632-638 relates to tubular carbon whiskers. Said whiskers are grown by the decomposition of gaseous hydrocarbons on submicron catalytic particles at temperatures above 900°C. According to the teaching of this article carbon filaments are invariably tubular.

Further, European patent application no. 0 136 497 discloses a process for preparing fine carbon fibers in which a mixed gas consisting of a gas of an organic metal compound and a carrier gas is reacted at an elevated temperature. The actually used temperature used in said process is stated to be at from 1010-1300°C.

**Summary of the Invention**

According to the present invention, it has now been found that high-performance carbon filaments (a single strand of carbonites as opposed to a carbon fiber made from a polymer fiber, for example) can be prepared by exposing a suitable thermostable support having deposited thereon substantially completely reduced monocrystalline metal particles to a carbon containing gas mixture.

The diameter of the metal particles is greater than about 5 nanometer (nm), and preferably greater than about 10 nm. The support and metal particles are exposed to a temperature of from about 250° up to about 700°C to 800°C. The upper temperature range of 700°C to 800°C is contingent upon the experimental conditions such as the nature of the catalyst, the carbon delivering gas, and the like.

The carbon filaments of the invention are characterized by a unique crystalline graphitic structure and a morphology defined by a fishbone-like arrangement of the graphitic layers along the axis of the filaments. The carbon containing gas may be any suitable gas, such as carbon monoxide and hydrogen, methane or other hydrocarbons, or mixtures thereof.

Further, the invention resides in a method for the preparation of carbon filaments, comprising the steps of exposing a thermostable support having deposited thereon substantially completely reduced monocrystalline metal particles to a carbon containing gas at a temperature of from about 250°C up to about 700°C to 800°C for a period of time sufficient to form carbon filaments of a desired

dimension on the support, the upper temperature limits being contingent upon the stability of a metal carbide which is formed preceding the nucleation of filamentous carbon, said filaments being characterized by a crystalline graphitic structure and a morphology defined by a fishbone-like arrangement of the graphite layers along the axis of the filaments, and thereafter separating the carbon filaments from the support and/or the metal particles.

#### Description of the Drawings

Hereinafter, the invention will be described in detail with reference to the accompanying drawings wherein:

Fig. 1 is a graph showing the magnetization in arbitrary units vs. time.

Fig. 2 is an idealized view of a carbon filament showing its morphological features.

#### Detail Description of the Invention

In the method of the present invention, the metal particles to be used must have a reasonable affinity to carbon. By this it is meant that the metal particles must have a reasonable ability to transport carbon since the rate of carbon filament growth is equal to the rate of transport of carbon through the metal particle. For this reason, platinum or palladium particles can be used. However, copper which has a low affinity to carbon, for example, is unsuitable. Preferably, the metal particles to be used must be capable of forming unstable metal carbides. Particularly good results are obtained when iron, cobalt or nickel, or alloys of these metals are used as the metal particles.

The minimum diameter of the metal particles suitable for filament growth is about 5 nm. It has been found that when smaller particles are used, no satisfactory carbon filament growth can take place. Preferably, the minimum diameter of the metal particle is about 10 nm. Metal particles with a diameter larger than 10 nm are particularly suitable for filament growth.

It is of importance that the metal particles should be substantially fully reduced since metal particles which are not fully reduced have an oxidic contact with the thermally stable support which inhibits the growth of carbon filaments. Furthermore, the metal particles must not contain any grain boundaries, i.e., the metal particles must not contain any boundary surfaces of crystals having different crystal orientations.

Without wishing to be limited in any way, it is believed that the mechanism of the growth of the carbon filaments is the following. The carbon containing gas is decomposed to carbon and adsorbed at the metal-gas interface of the metal particles.

Subsequently, the carbon atoms taken up into the surface of the metal particles migrate into the metal and either react with the metal to form a carbide, or dissolve into the metal.

With ferromagnetic metals, the formation of a carbide can be assessed by measuring magnetization. Since the saturation magnetization of nickel, iron and cobalt carbides is either zero or appreciably lower than that of the pure metal, the drop in magnetization exhibited on exposure of the metal particles to the carbon containing gas demonstrates that the carbon has reacted to form metal carbide.

After the formation of the metal carbide, or after the dissolution of carbon into the metal, the nucleation of carbon at the interface between the metal and the substrate proceeds. The graphite nuclei subsequently grows into carbon filaments. With ferromagnetic metals, magnetization passes through a minimum on exposure of the metal particles to a carbon containing gas. This change in magnetization can be interpreted to be due to the nucleation of graphite after the formation of the metal carbides by reaction of the metal with the carbon containing gas.

With metals that cannot react to form bulk carbides, the nucleation of graphite proceeds from carbon atoms dissolved in the metal. Since the amount of carbon that can be dissolved into metals not capable of reacting to form a bulk carbide is relatively small, the nucleation of graphite at the interface with the substrate proceeds presumably more slowly.

The growth of graphite layers from the metal particles leads to the formation of carbon filaments. Presumably, the graphite layers are formed by epitaxial growth at the interface of the metal or perhaps metal carbide surface and the support. Due to the interaction between the graphite crystallites and the metal particle, the diameter of the growing carbon filament remains substantially equal to the diameter of the metal particle. The growth of graphite layers at the metal-carbon interface is determined by the rate of transport of carbon through the metal particle. Consequently, the growth of graphite at the metal-graphite interface is more rapid at those sites which are closer to the metal-gas interface and, conversely, the growth of graphite at the metal-graphite interface is less rapid at those sites which are more distant from the metal-gas interface. Thus, the different rates of transport of carbon through the metal particles leads to different rates of growths of graphite at the metal-graphite interface resulting in a fishbone-like structure.

Stated another way, the metal particle is pushed up by graphite layers which are sequentially produced at the interface. However, the rate at

which carbon atoms are being transported varies at different sites of the interface. This is due to the fact that the rate of migration of carbon atoms through the metal particles determines the rate of growth of the carbon filaments. Since the length of the path to be travelled by carbon atoms migrating from different sites of the metal-gas interface to the metal-carbon interface varies, the number of carbon atoms per unit time arriving at the interface varies according to the relative locations. As a result, stacked graphite layers are formed, leading to the desired fishbone-like structure.

The number of carbon filaments growing per unit area of support can be varied by changing the number of metal particles, per unit area of support surface. A small number of metal particles per unit area of support surface results in a low density of carbon filaments on the support surface, whereas a large number of metal particles per unit area of support surface leads to a dense network of carbon filaments.

The size of the metal particles can be controlled by, for instance, sintering the metal particles at an elevated temperature. Consequently, the diameter of the carbon filaments can be controlled by controlling the size of the metal particles. It is important that the size distribution of the metal particles should preferably be in a narrow range so that the filaments produced will exhibit a correspondingly uniform diameter distribution.

The supported metal particles used in the method according to the present invention can in principle be produced using techniques which are known for the production of supported metal catalysts, and in principle, the same carrier materials, e.g. silica, alumina, and other inert support materials can be used provided that such support materials exhibit desirable metal particle-support interactions to promote the formation of carbon filaments from the supported metal particles.

The metal particle-support systems must satisfy certain requirements, however, and these should be taken into account, in particular those factors which control the diameter of the particles and their distribution. Only those methods and supports which produce metal particles of substantially uniform diameters are suitable for the purposes of this invention. It will be obvious, of course, that for certain applications, the particle size may vary to produce filaments having a somewhat non-uniform diameter distribution.

In the production of the metal particle-support systems suitable for use in the method according to the present invention, it is of importance to achieve a high loading with completely reduced metal particles. When the density of metal particles per unit area of the support is too high, the carbon filaments produced are shorter in length than when

the density of the metal particles per unit area is low. Accordingly, the length of filament growth on the support can be controlled by properly adjusting the distribution density of metal particles on the support.

One suitable method of producing metal particle-support systems according to the present invention is by vapor deposition of a metal, for example, nickel, on a non-metallic support made of, for example, alumina, followed by a thermal treatment of the support (with the metal particles adhered to the support) in a non-oxidizing atmosphere. Another suitable method is the well-known deposition-precipitation technique followed by an appropriate reduction treatment, which produces the desired size of metal particles. Other well-known techniques for producing metal particle-support systems can be used to advantage such as, for example, solution deposition; electro-deposition; colloidal-metal deposition, and the like.

A particularly suitable technique is the decomposition of a gaseous carbonyl of the desired metal, or a mixture of gaseous carbonyls of the desired metal, or of gaseous metal-organic compounds that can be thermally decomposed. If such procedures are carried out using the support with a fluid-bed reactor, a particular advantage is that both the supported metal-particle system can be produced and the carbon filaments can be formed and grown in the same reactor.

In the method according to the invention, the thermodynamic conditions defined by the correct temperature and pressure and composition of the different reactants and resulting products play an important role in the filament growth process. In particular, the choice of temperature is preferably from about 250° up to about 700°C to 800°C but must not be higher than that at which the corresponding metal carbides formed are still stable.

It is noted that the phenomenon of the formation of carbon deposits has been extensively investigated and described in the literature. Thus, various forms of carbon deposits, including the filamentary form, are described in publications by Baker et al. and Rostrup Nielson (*Journal of Catalysis*, 26, 51-62 (1972) and *Journal of Catalysis*, 48, 155-165 (1977)). These publications are concerned, however, with research on conventional supported metal catalysts which provide for a large support surface area at a low metal particle loading on the support surface.

Thus, the authors, in the aforementioned publications, determined that the carbon microcrystallites in the carbon filaments had a low degree of orientation and, hence, the mechanical strength was weak. Measurements of the gas phase in equilibrium with the carbon filaments were interpreted to indicate that the thermodynamic stability of the

carbon in the filaments was appreciably less than that of graphite. This also was considered to indicate that the crystallinity of the filaments was low.

Surprisingly, the mechanical strength of the carbon filaments of the present invention is very high. In fact, the strength of the filaments is so high that in the use of alumina as the support structure, the filaments were growing into the alumina causing a complete disintegration of the support.

It can be established, especially by the selected area electron diffraction method, that the carbon filaments contain symmetrically arranged or stacked crystalline graphite layers forming the herein-before described fishbone-like structure. The presence of stacked graphite layers, their orientation, and the resulting mechanical strength have thus far not been recognized by investigators in this area of endeavor.

In the method of the present invention, growth of the carbon filaments on the metal particle-support system leads to a dense network of carbon filaments containing the residues of the disintegrated support and exhibiting a metal particle at the growth end of the filament. During the growth of the filaments, it is important that the reactor is sufficiently large to accommodate an appreciable increase in volume of the growing filaments. The reactor may be of any suitable type, the choice of which is generally determined by the specific configuration (length, density, etc.) of the carbon filament bundles obtained. To avoid any spacial volume limitations, a fluid-bed reactor could be used. In such a device, the support and metal particles are suspended in a fluidized state by means of a flowing gas which includes a source of carbon as a raw material for the growth of carbon filaments on the support.

In the method according to the invention, a so-called secondary growth of the diameter of the carbon filaments can be accomplished by exposing the formed filaments having the fishbone like structure to a temperature above about 900°C in the presence of a carbon-containing gas. It is conceivable that the secondary carbon growth on the external surface of the filament may give origin to a composite filament structure of unique mechanical strength. Such a structure will be somewhat analogous to a plywood composite. At the higher temperatures, further growth of the filaments in the longitudinal direction does not take place, but carbon is deposited on the outer surfaces of the filaments thereby enlarging the diameter of the filaments. To maintain a reasonably uniform diameter of the filaments, the accessibility of the filaments to the gaseous phase must not differ markedly within the reactor. This condition may be particularly well satisfied in a fluidized-bed reactor in which an excellent accessibility of the filaments

to the gaseous phase can take place.

If desired, the filaments formed in accordance with the present invention can be separated from the support and/or the metal particles by a chemical or a mechanical treatment. For example, if the support is formed of silica, it can be rapidly dissolved in an alkaline solution. Likewise, if both the metal particles and the support must be removed, the use of an alumina support is attractive in that an acid solution leads to the dissolution of both the alumina support and the metal particles.

According to a further embodiment of the invention, the isolated carbon filaments (without the support and/or metal particles) can be combined with a molten polymer or monomer, or mixtures thereof, which is subsequently polymerized to form a filament-reinforced polymer composite. If the filaments are randomly oriented in the composite, the filament impregnated materials will be stronger in every direction and will not exhibit a more pronounced mechanical strength in any particular direction.

When a high mechanical strength in one direction is required, another procedure according to the invention can be utilized. After combining the carbon filaments with a molten polymer or monomer, or mixture thereof, the carbon filaments are dispersed in the molten mass and the suspension thus obtained is subjected to a mechanical shear whereby the carbon filaments are oriented in a direction parallel to the direction of polymer flow. Subsequent solidification or polymerization fixes the orientation of the carbon filaments within the solidified polymer.

Filaments made at temperatures of from about 250°C and up to about 700°C to 800°C display a resistance to compression that is much higher than that to tension. Even though these filaments have a high resistance to compression, they can still be used to great advantage to produce composites having a high tensile strength. To obtain the objective, a mixture of these filaments and polymeric material can be subjected to pressure prior to solidification of the mixture to form a polymer composite having higher tensile strength.

According to another aspect of the invention, ferromagnetic particles, such as nickel, metallic iron or alloys thereof can be used to grow carbon filaments. These metal particles are located at the tip of the filaments. Since these particles are ferromagnetic, the filaments will become oriented in an electric and/or a magnetic field. When filaments having ferromagnetic particles at their ends, or when filaments having ferromagnetic particles at their ends in combination with molten polymers, monomers or mixtures thereof, are exposed to an electric and/or magnetic field, oriented filaments are produced, or oriented fibers are produced dur-

ing setting of the polymer to produce a composite with oriented filaments. In the case of composites suitable procedures known to the manufacturer of magnetic tapes can be used.

According to still another embodiment of the invention, after the filaments have been formed, the temperature is greatly increased to above about 1000°C and up to about 1800°C. In this way, a reorientation of the crystals in the filaments is accomplished, resulting in enhanced crystallinity and improved physical properties of the filament.

When ferromagnetic metal particles are used for the growth of the carbon filaments, these filaments can be oriented in a parallel relationship with each other by placing the substrate in an electric or magnetic field having the desired strength to promote growth of the fibers in a parallel manner. As herein before stated, when filaments of a greater diameter are desired, relatively thin filaments with a fishbone like structure provide an outer surface which is readily accessible to gas molecules, so that the filaments can be exposed to a carbon-containing gas at an elevated temperature of from about 900° to about 1100°C, i.e., a temperature at which the filaments no longer grow in a longitudinal direction. After completion of the treatment at such elevated temperature, the temperature can be further raised in excess of about 1100° and more advantageously up to about 1800°C. In view of the fact that the ferromagnetism decreases and finally disappears at elevated temperatures, it is desirable to keep the ends of the filaments, where the ferromagnetic particles are present, at a lower temperature.

According to a further embodiment of the invention, stretched carbon fibers of the prior art, or filaments of the invention can be subjected to a high temperature in a narrow zone, as viewed in the longitudinal direction, of the fibers or filaments, which narrow temperature zone is swept over the fibers or filaments. Preferably, this narrow high temperature zone is produced by using a high-frequency generator. This method therefore is analogous to zone melting used for the production and purification of silicon monocrystals.

The carbon filaments produced by the method according to this invention can be used for all purposes hitherto known for (high performance) carbon filaments. More particularly they can be used, by virtue of their excellent mechanical and electrochemical properties, for the manufacture of electrodes for electrochemical applications. For this purpose, the fibers are preferably grown using a flat substrate in a restricted volume, optionally in the presence of an electric or magnetic field. As a result of the limited volume available, the resulting network of filaments will be very dense. The metal tips can subsequently be removed by treatment

with an acid since the carbon filaments do not dissolve in an acid. If after the formation of the filaments the temperature is raised preferably to above about 900°C, while maintaining the atmosphere of the carbon-containing gas mixture, carbon deposits will grow on the filaments so that an extremely dense and monolithic block of graphitized carbon filaments is produced.

10 Example 1 - Preparation of Ni-on-silica Substrate Precursor

2,475.7 g  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 1,200 g of urea were dissolved into 10 liters of water. Subsequently 15 500 g of silica of a surface area of 300 m<sup>2</sup>/g were suspended into the solution (Degussa.). The suspension was heated to 368°K under vigorous stirring and kept for 24 hours at that temperature. After that period the dissolved nickel was virtually 20 completely precipitated. The green silica loaded by the precipitated nickel was separated from the liquid and thoroughly washed. Next it was dried at 403°K for 24 hours. The dry mass was subsequently pressed to tablets of a diameter of about 1.5 mm and a thickness of about 4 mm. The tablets were cut by a knife into particles of 0.15 mm to 0.30 mm. 1 to 3 g of the above nickel-loaded particles were brought into a tubular quartz reactor whose internal diameter was 10 mm. The 25 material was dehydrated in a flow of 10% H<sub>2</sub> in nitrogen for at least 72 hours at 723°K. To raise the degree of reduction the nickel particles were 30 finally kept in the H<sub>2</sub>/N<sub>2</sub> flow for one hour at 950°K.

35 Example 2 - Preparation of an Iron-on- $\delta$ -Alumina Substrate Precursor

500 g of alumina of a surface area of 80 m<sup>2</sup>/g 40 (Degussa C) were suspended into 3 liters of water. The temperature of the suspension was raised to 353°K. Subsequently a soda solution and a solution of 3,615 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 5 liters of water were injected into the suspension below the 45 level of the liquid through tubes of an internal diameter of 2 mm. The rate of the injection of the soda solution was controlled so as to keep the pH at a constant level of 6.0. After completion of the injection of the iron solution the brown alumina loaded with the iron was separated from the carrier and thoroughly washed. The washed material was 50 dried at 393°K for 24 hours. Subsequently the dried mass was pressed into tablets of a diameter of about 1.5 m and a thickness of about 4 mm. The tablets were cut by a knife into particles of 0.15 mm to 0.30 mm. 1 to 3 g of the particles thus obtained were loaded into a tubular quartz reactor of an internal diameter of 10 mm. The iron was 55

reduced by keeping the particles in a flow of 10% H<sub>2</sub> in argon at 873°K for at least 10 hours. The reduction was completed by keeping the mass in the H<sub>2</sub>/Argon flow at 950°K for at least one hour.

### Example 3-Growth of Carbon Filaments

Carbon filament growth was accomplished by introducing gas mixtures typically containing from about 1 to about 10 volume percent of a carbon-bearing gas. The gas mixture was fed to a quartz reactor having an inside diameter of 10 millimeters and containing from about 1 to about 3 grams of a pelleted catalyst. The catalyst pellets had a diameter of from about 0.15 mm to 0.30 millimeters.

The behaviour of nickel catalyst particles concurrent with growth of filamentous carbon was studied using freshly reduced 50 weight% Ni/SiO<sub>2</sub> catalyst, reduced at 870°K. A gas mixture of 10 Vol.% methane in nitrogen was introduced into the quartz reactor at a flow rate of 0.8 cm<sup>3</sup>/s. Methane was chosen as the source of carbon to prevent Ostwald ripening of the nickel particles due to transport via Ni(CO)<sub>4</sub>.

Magnetization measurements were made as a function of time to gain an insight into the growth mechanism of the filamentous carbon. The magnetization was followed during carbonization at three different temperatures, namely 576°K, 596°K, and 611°K. Initially a decrease of the magnetization was observed. Having passed through a minimum, the magnetization increased gradually up to 70% of the original value, as shown in Fig. (2). These changes in magnetization were associated with the formation of a metal carbide preceding the nucleation of filaments of graphitic carbon. Electron microscopy revealed that only nickel particles with a diameter larger than 10 nm were involved exclusively in filament growth. The observation of the gradual increase of magnetization indicates that after nucleation of filamentous carbon the carbon content of the catalyst particles is significantly lower than the carbon content at the early stages of carbonization.

In a similar experiment, a mixture of CO/H<sub>2</sub> at a ratio of 0.5/1 was employed. The growth of graphitic filaments was observed. The filaments were observed to have relatively electron-transparent canals along their axes and a textured structure. Nickel particles at the tip of these filaments exhibited a cone-shaped appearance. Selected area diffraction experiments were performed on a filament having a diameter of 70 nm. The filament was striking in its appearance by its straightness. Such a filament was especially suited for analysis of its carbon microstructure, as it contains only one well-defined direction of its axis. It was noted that two distinct orientations of the graphite layers were

present. These two different orientations were localized on opposite sides of the filament axis. This microstructure can be represented by a fishbone like arrangement of the graphite basal planes along the filament axis as shown in Fig (2).

### Claims

1. A carbon filament having a crystalline graphitic structure and a morphology defined by a fishbone-like arrangement of symmetrically stacked graphite layers along the axis of the filament.
2. A carbon filament according to claim 1, wherein said filament is formed by the growth of graphite layers at an interface of a substantially completely reduced monocrystalline metal particle and a thermostable support, said metal particle having a size of greater than 5 nanometers.
3. A carbon filament according to claim 1 or 2, comprising the metal particle.
4. A carbon filament according to claim 2 or 3, wherein the metal particle has a size of greater than 10 nanometers, and wherein the diameter of the carbon filament is substantially equal to the diameter of the metal particle.
5. A carbon filament according to one of the claims 2-4, wherein the metal particle is selected from iron, cobalt, nickel or alloys thereof.
6. A carbon filament according to one of the claims 1-5, including a secondary growth of carbon on the external surface of the filament.
7. A method for the preparation of carbon filaments having a crystalline graphitic structure and a morphology defined by a fishbone-like arrangement of symmetrically stacked graphite layers along the axis of the filaments, comprising the steps of exposing a thermostable support having deposited thereon substantially completely reduced monocrystalline metal particles to a carbon-containing gas at a temperature from about 250°C up to about 700-800°C for a period sufficient to form filaments of a desired dimension on the support, the upper temperature limit being contingent upon the stability of a metal carbide which is formed preceding the nucleation of filamentous carbon, and thereafter separating the carbon filaments from the support and/or the metal particles.

8. A method according to claim 7, wherein the size of the metal particles is adjusted to control the diameter of the carbon filaments, and wherein the distribution density of said metal particles is adjusted to control the distribution density of said carbon filaments and the length of filament growth.

9. A method according to claim 7 or 8, wherein metal particles having a particle size of at least about 5 nm are used.

10. A method according to one of the claims 7-9, wherein metal particles having a particle size of at least about 10 nm are used.

11. A method according to one of the claims 7-10, wherein metal particles are used which are able to form unstable metal carbides.

12. A method according to one of the claims 7-11, wherein metal particles are used which are ferromagnetic.

13. A method according to one of the claims 7-12, wherein the metal particles are selected from the group iron, cobalt, nickel, and alloys thereof.

14. A method according to one of the claims 7-13, wherein the carbon filaments are subsequently subjected to a controlled amount of a carbon-containing gas at a temperature in the range of from 900-1100°C, to effect a secondary growth of carbon on the external surface of the filament.

15. A method according to one of the claims 7-14, wherein the carbon filaments are subsequently subjected to a temperature of from 1100-1800°C in the absence of a carbon-containing gas, to effect a reorientation of the crystals in the carbon filament.

16. A method according to one of the claims 7-15, wherein said support is selected from non-metallic materials, metals, not forming bulk carbides metal alloys, metal oxides, metal carbides, metal sulfides, and carbon.

17. A method according to one of the claims 7-16, wherein said support is selected from silica, alumina, and other inert support materials, with the proviso that said materials exhibit desirable metal particle-support interactions to promote the formation of carbon filaments from the supported metal particles.

5                   18. A method for the preparation of reinforced polymers, comprising the steps of impregnating or dispersing the carbon filaments according to one of the claims 1-6 with a molten polymer, a monomer, or a mixture thereof, and subsequently polymerizing or solidifying the composition obtained.

10                 19. A method according to claim 18, wherein the carbon filaments are dispersed in a molten polymer or monomer, or mixtures thereof, and wherein the suspension thus obtained is subjected to a shear force before the polymerizing or solidifying step.

15                 20. A method according to claim 18, wherein the carbon filaments with ferromagnetic particles attached at the end of the filaments are dispersed in a molten polymer or monomer, or mixtures thereof, and wherein the suspension is subjected to an applied external electric and magnetic field or a combination of an electric and magnetic field during solidification.

20                 21. A reinforced polymer produced by the method of claims 18-20.

25                 22. A method for the production of an electrode, comprising the steps of subjecting the carbon filaments according to one of the claims 1-6 to a temperature above about 900°C, while maintaining the atmosphere of the carbon-containing gas mixture to enhance the growth of carbon deposits on the filaments to form a dense and homogenous block of carbon.

30                 23. A carbon electrode, obtained by the method of claim 22.

35                 40                 Patentansprüche

40                 1. Kohlenstoff-Filament mit einer kristallinen graphitischen Struktur und einer Morphologie, die durch eine fischgrätenartige Anordnung von symmetrisch gestapelten Graphitschichten entlang der Achse des Filaments definiert ist.

45                 2. Kohlenstoff-Filament nach Anspruch 1, worin das Filament durch das Wachstum von Graphitschichten an einer Grenzfläche eines im wesentlichen vollständig reduzierten, monokristallinen Metallteilchens und eines hitzestabilen Trägers gebildet ist, wobei das Metallteilchen eine Größe von mehr als 5 Nanometer aufweist.

50                 55                 3. Kohlenstoff-Filament nach Anspruch 1 oder 2, umfassend das Metallteilchen.

4. Kohlenstoff-Filament nach Anspruch 2 oder 3, worin das Metallteilchen eine Größe von mehr als 10 Nanometer aufweist und worin der Durchmesser des Kohlenstoff-Filaments im wesentlichen gleich wie der Durchmesser des Metallteilchens ist. 5

5. Kohlenstoff-Filament nach einem der Ansprüche 2 bis 4, worin das Metallteilchen aus Eisen, Kobalt, Nickel oder Legierungen davon ausgewählt ist. 10

6. Kohlenstoff-Filament nach einem der Ansprüche 1 bis 5, einschließlich einem Sekundärwachstum von Kohlenstoff auf der äußeren Oberfläche des Filaments. 15

7. Verfahren zur Herstellung von Kohlenstoff-Filamenten mit einer kristallinen graphitischen Struktur und einer Morphologie, die durch eine fischgrätenartige Anordnung von symmetrisch gestapelten Graphitschichten entlang der Achse der Filamente definiert ist, umfassend die Schritte des Behandlens eines hitzestabilen Trägers, auf dem im wesentlichen vollständig reduzierte, monokristalline Metallteilchen abgeschieden sind, mit einem kohlenstoffhaltigen Gas bei einer Temperatur von etwa 250 °C bis zu etwa 700-800 °C für eine ausreichende Zeitspanne, um Filamente einer gewünschten Dimension auf dem Träger zu bilden, wobei die obere Temperaturlinie durch die Stabilität eines Metalcarbids bedingt ist, das vor der Nukleation von filamentartigem Kohlenstoff gebildet wird, und des anschließenden Abtrennens der Kohlenstoff-Filamente vom Träger und/oder den Metallteilchen. 20

8. Verfahren nach Anspruch 7, worin die Größe der Metallteilchen reguliert wird, um den Durchmesser der Kohlenstoff-Filamente zu kontrollieren, und worin die Verteilungsdichte der Metallteilchen reguliert wird, um die Verteilungsdichte der Kohlenstoff-Filamente und die Länge des Filamentwachstums zu kontrollieren. 40

9. Verfahren nach Anspruch 7 oder 8, worin man Metallteilchen mit einer Teilchengröße von mindestens etwa 5 Nanometer verwendet. 50

10. Verfahren nach einem der Ansprüche 7 bis 9, worin man Metallteilchen mit einer Teilchengröße von mindestens etwa 10 Nanometer verwendet. 55

11. Verfahren nach einem der Ansprüche 7 bis 10, worin man Metallteilchen verwendet, die in der Lage sind, instabile Metalcarbide zu bilden.

12. Verfahren nach einem der Ansprüche 7 bis 11, worin man Metallteilchen verwendet, die ferromagnetisch sind.

13. Verfahren nach einem der Ansprüche 7 bis 12, worin die Metallteilchen aus der Gruppe Eisen, Kobalt, Nickel und Legierungen davon ausgewählt werden.

14. Verfahren nach einem der Ansprüche 7 bis 13, worin die Kohlenstoff-Filamente anschließend mit einer kontrollierten Menge eines kohlenstoffhaltigen Gases bei einer Temperatur im Bereich von 900-1100 °C behandelt werden, um ein Sekundärwachstum von Kohlenstoff an der äußeren Oberfläche des Filaments zu bewirken.

15. Verfahren nach einem der Ansprüche 7 bis 14, worin die Kohlenstoff-Filamente anschließend bei einer Temperatur im Bereich von 1100-1800 °C in Abwesenheit eines kohlenstoffhaltigen Gases behandelt werden, um eine Reorientierung der Kristalle im Kohlenstoff-Filament zu bewirken.

16. Verfahren nach einem der Ansprüche 7 bis 15, worin der Träger aus nichtmetallischen Materialien, Metallen, nicht Carbide in großen Mengen bildenden Metalllegierungen, Metalloxiden, Metalcarbiden, Metallsulfiden und Kohlenstoff ausgewählt wird.

17. Verfahren nach einem der Ansprüche 7 bis 16, worin der Träger aus Siliciumoxid, Aluminiumoxid und anderen inerten Trägermaterialien ausgewählt wird, unter der Voraussetzung, daß die Materialien günstige Metallteilchen-Träger-Wechselwirkungen zeigen, um die Bildung von Kohlenstoff-Filamenten auf den getragenen Metallteilchen zu fördern.

18. Verfahren zur Herstellung von verstärkten Polymeren, umfassend die Schritte des Imprägnierens oder Dispergierens der Kohlenstoff-Filamente nach einem der Ansprüche 1 bis 6 mit einem geschmolzenen Polymer, einem Monomer oder einem Gemisch daraus und des anschließenden Polymerisierens oder Verfestigens der erhaltenen Zusammensetzung.

19. Verfahren nach Anspruch 18, worin die Kohlenstoff-Filamente in einem geschmolzenen Polymer oder Monomer oder Gemischen daraus dispergiert werden, und worin die so erhaltene Suspension vor dem Polymerisierungs-

oder Verfestigungsschritt mit einer Scherkraft behandelt wird.

20. Verfahren nach Ansprache 18, worin die Kohlenstoff-Filamente mit am Ende der Filamente befindlichen ferromagnetischen Teilchen in einem geschmolzenen Polymer oder Monomer oder Gemischen daraus dispergiert werden, und worin die Suspension während der Verfestigung mit einem angelegten elektrischen und magnetischen Feld oder einer Kombination eines elektrischen und magnetischen Feldes behandelt wird.

21. Verstärktes Polymer, hergestellt durch das Verfahren nach einem der Ansprüche 18 bis 20.

22. Verfahren zur Herstellung einer Elektrode, umfassend die Schritte des Behandlens der Kohlenstoff-Filamente nach einem der Ansprüche 1 bis 6 bei einer Temperatur von über etwa 900 °C, während die Atmosphäre des kohlenstoffhaltigen Gasgemisches beibehalten wird, um das Wachstum der Kohlenstoffabscheidungen auf den Filamenten zu erhöhen, so daß ein dichter und homogener Kohlenstoffblock gebildet wird.

23. Kohlenstoff-Elektrode, erhalten durch das Verfahren nach Anspruch 22.

**Revendications**

1. Filament de carbone ayant une structure cristalline graphitique et une morphologie définie par un arrangement en arête de poisson constitué par des couches de graphite empilées symétriquement le long de l'axe du filament.
2. Filament de carbone selon la revendication 1, dans lequel le filament est formé par croissance de couches de graphite à l'interface d'une particule monocristalline d'un métal pratiquement complètement réduit et d'un support thermostable, la particule de métal ayant des dimensions supérieures à 5 nanomètres.
3. Filament de carbone selon l'une des revendications 1 ou 2 comprenant la particule de métal.
4. Filament de carbone selon l'une des revendications 2 ou 3, dans lequel la particule de métal a des dimensions supérieures à 10 nanomètres et dans lequel le diamètre du filament de carbone est pratiquement égal au diamètre de la particule de métal.
5. Filament de carbone selon l'une des revendications 2 à 4, dans lequel la particule de métal est choisie dans le groupe formé par le fer, le cobalt, le nickel et leurs alliages.
6. Filament de carbone selon l'une des revendications 1 à 5 comprenant une croissance secondaire de carbone sur la surface externe du filament.
7. Méthode de préparation de filaments de carbone ayant une structure cristalline graphitique et une morphologie définie par un arrangement en arête de poisson constitué de couches de graphite empilées le long de l'axe des filaments comprenant une étape consistant à exposer un support thermostable sur lequel sont déposées des particules monocristallines de métal pratiquement complètement réduit à un gaz contenant du carbone, à une température comprise entre environ 250 °C et environ 700-800 °C pendant un temps suffisant pour former des filaments de la dimension désirée sur le support, la température limite supérieure dépendant de la stabilité d'un carbure métallique qui se forme avant la nucléation de carbone filamentaire, et une étape ultérieure consistant à séparer les filaments de carbone du support et/ou des particules de métal.
8. Méthode selon la revendication 7, dans laquelle la dimension des particules de métal est choisie de façon à régler le diamètre des filaments de carbone et dans laquelle la densité de répartition des particules de métal est choisie de façon à régler la densité de répartition des filaments de carbone et la croissance en longueur des filaments.
9. Méthode selon l'une des revendications 7 ou 8, dans laquelle on utilise des particules de métal ayant des dimensions d'au moins environ 5 nanomètres.
10. Méthode selon l'une des revendications 7 à 9, dans laquelle les particules de métal ont des dimensions d'au moins 10 nanomètres.
11. Méthode selon l'une des revendications 7 à 10, dans laquelle les particules de métal utilisées sont capables de former des carbures métalliques instables.
12. Méthode selon l'une des revendications 7 à 11, dans laquelle les particules de métal utilisées sont ferromagnétiques.

13. Méthode selon l'une des revendications 7 à 12, dans laquelle les particules de métal sont choisies dans le groupe formé par le fer, le cobalt, le nickel et leurs alliages.

14. Méthode selon l'une des revendications 7 à 13, dans laquelle les filaments de carbone sont ultérieurement soumis à une quantité réglée d'un gaz contenant du carbone à une température comprise entre 900 et 1100 °C pour effectuer une croissance secondaire de carbone sur la surface externe du filament.

15. Méthode selon l'une des revendications 7 à 14, dans laquelle les filaments de carbone sont ultérieurement soumis à une température de 1100 à 1800 °C en l'absence de gaz contenant du carbone, pour effectuer une réorientation des cristaux dans le filament de carbone.

16. Méthode selon l'une des revendications 7 à 15, dans laquelle le support est choisi parmi les matériaux non-métalliques, les métaux, les alliages ne formant pas de masse de carbures, les oxydes métalliques, les carbures métalliques, les sulfures métalliques et le carbone.

17. Méthode selon l'une des revendications 7 à 16, dans laquelle le support est choisi parmi la silice, l'alumine et autres matériaux de support inertes, étant entendu que lesdits matériaux présentent les interactions (particules de métal-support) souhaitables pour provoquer la formation de filaments de carbone à partir des particules de métal sur le support.

18. Méthode de préparation de polymères renforcés comprenant les étapes consistant à imprégner et disperser les filaments de carbone selon l'une des revendications 1 à 6 avec un polymère fondu, un monomère ou un mélange de ceux-ci, et ensuite à polymériser ou solidifier la composition obtenue.

19. Méthode selon la revendication 18, dans laquelle les filaments de carbone sont dispersés dans un polymère fondu, un monomère ou un mélange de ceux-ci et la suspension obtenue est soumise à une force de cisaillement avant l'étape de polymérisation ou solidification.

20. Méthode selon la revendication 18, dans laquelle les filaments de carbone, sur l'extrémité desquels sont fixées des particules ferromagnétiques, sont dispersés dans un polymère fondu, un monomère ou leurs mélanges et la suspension est soumise à un champ électrique ou magnétique appliqué de l'extérieur ou à une combinaison de champs électrique et magnétique, au cours de la solidification.

5 21. Polymère renforcé préparé selon la méthode de l'une des revendications 18 à 20.

10 22. Méthode pour la fabrication d'une électrode comprenant les étapes consistant à soumettre des filaments de carbone selon l'une des revendications 1 à 6 à une température supérieure à environ 900 °C tout en maintenant une atmosphère de gaz contenant du carbone, de façon à augmenter la croissance des dépôts de carbone sur les filaments et à former un bloc de carbone dense et homogène.

15 23. Electrode de carbone obtenue par la méthode de la revendication 22.

20

25

30

35

40

45

50

55

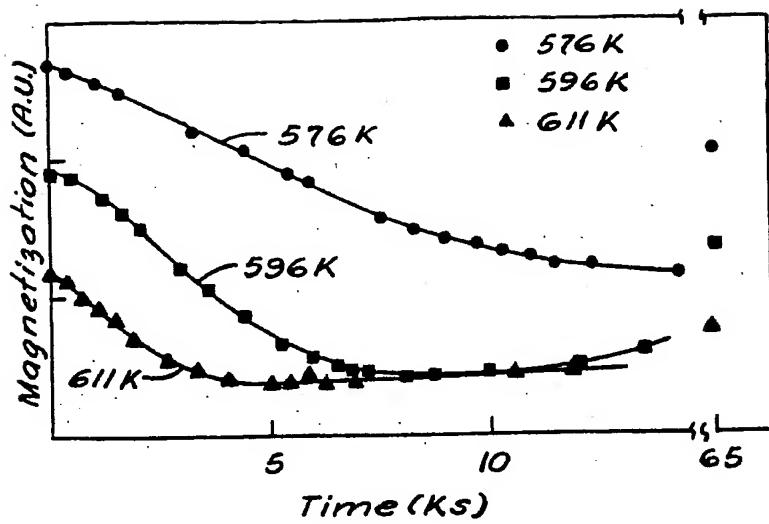


Fig. 1

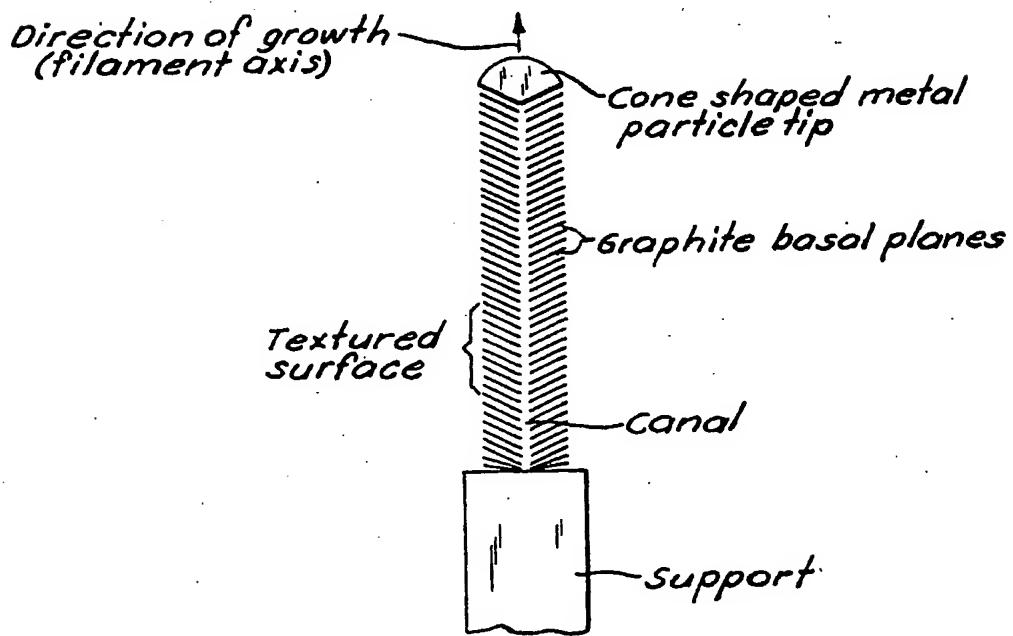


Fig. 2

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

**BLACK BORDERS**

**IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

**FADED TEXT OR DRAWING**

**BLURRED OR ILLEGIBLE TEXT OR DRAWING**

**SKEWED/SLANTED IMAGES**

**COLOR OR BLACK AND WHITE PHOTOGRAPHS**

**GRAY SCALE DOCUMENTS**

**LINES OR MARKS ON ORIGINAL DOCUMENT**

**REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

**OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**